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*Indian Standard*

METHODS OF CHEMICAL ANALYSIS  
OF ALUMINIUM AND ITS ALLOYS

( Revised )

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May 1964

# Indian Standard

## METHODS OF CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

### ( Revised )

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## CONTENTS

	PAGE
0. FOREWORD ... ..	5
1. SCOPE ... ..	7
2. SAMPLING ... ..	7
3. GENERAL ... ..	7
4. QUALITY OF REAGENTS ... ..	7
5. DETERMINATION OF SILICON BY THE MOLYBDENUM YELLOW (PHOTOMETRIC) METHOD (FOR SILICON CONTENT BETWEEN 0.02 TO 0.3 PERCENT) ... ..	8
6. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD (FOR SILICON CONTENT OVER 0.3 PERCENT) ... ..	9
7. DETERMINATION OF LEAD BY THE SULPHIDE (COLORIMETRIC) METHOD ... ..	12
8. DETERMINATION OF IRON BY THE O-PHENANTHROLINE (PHOTO- METRIC) METHOD (FOR IRON CONTENT BETWEEN 0.03 TO 0.10 PERCENT) ... ..	12
9. DETERMINATION OF IRON BY THE TITANOUS CHLORIDE (VOLUMETRIC) METHOD (FOR IRON CONTENT BETWEEN 0.01 TO 2.0 PERCENT) ... ..	14
10. DETERMINATION OF COPPER BY THE DIETHYLDITHIOCAR- BAMATE (PHOTOMETRIC) METHOD (FOR COPPER CONTENT BELOW 0.1 PERCENT) ... ..	17
11. DETERMINATION OF COPPER BY THE IODOMETRIC METHOD (FOR COPPER CONTENT OVER 0.1 PERCENT) ... ..	19
12. DETERMINATION OF ZINC BY THE DITHIZONE (PHOTOMETRIC) METHOD (FOR ZINC CONTENT BELOW 0.1 PERCENT) ... ..	23
13. DETERMINATION OF ZINC BY MERCURIC THIOCYANATE METHOD ... ..	24
13.3 Gravimetric Method (for Zinc Content over 0.1 Per- cent) ... ..	26
13.4 Mercuric Thiocyanate (Volumetric) Method (for Zinc Content $\leq 0.1$ Percent) ... ..	27

	PAGE
14. DETERMINATION OF MANGANESE BY THE PERIODATE (PHOTOMETRIC) METHOD (FOR MANGANESE CONTENT BETWEEN 0.01 TO 0.1 PERCENT) ... ..	28
15. DETERMINATION OF MANGANESE BY THE PERSULPHATE ARSENITE METHOD (FOR CHROMIUM CONTENT UP TO 0.5 PERCENT) ... ..	29
16. DETERMINATION OF MANGANESE BY THE BISMUTHATE (ALTERNATE) METHOD (FOR MANGANESE CONTENT BETWEEN 0.1 TO 1.5 PERCENT) ... ..	31
17. DETERMINATION OF MAGNESIUM BY THE OXINE METHOD (FOR MAGNESIUM CONTENT BETWEEN 0.01 TO 12 PERCENT) ... ..	33
18. DETERMINATION OF MAGNESIUM BY THE ETHYLENEDIAMINE TETRA-ACETATE METHOD (FOR MAGNESIUM CONTENT BETWEEN 0.5 TO 11 PERCENT) ... ..	37
19. DETERMINATION OF NICKEL BY THE DIMETHYLGlyOXIME (GRAVIMETRIC) METHOD ... ..	40
20. DETERMINATION OF CHROMIUM BY THE PERSULPHATE OXIDATION (VOLUMETRIC) METHOD ... ..	41
21. DETERMINATION OF TIN BY THE IODOMETRIC METHOD ... ..	43
22. DETERMINATION OF ANTIMONY BY THE POTASSIUM IODIDE-THIOUREA (PHOTOMETRIC) METHOD ... ..	45
23. DETERMINATION OF TITANIUM BY THE HYDROGEN PEROXIDE (PHOTOMETRIC) METHOD ... ..	46



*Indian Standard*  
**METHODS OF CHEMICAL ANALYSIS  
OF ALUMINIUM AND ITS ALLOYS**  
*( Revised )*

**0. FOREWORD**

**0.1** This revised Indian Standard was adopted by the Indian Standards Institution on 1 October 1963, after the draft finalized by the Methods of Chemical Analysis Sectional Committee had been approved by the Structural and Metals Division Council.

**0.2** Aluminium industry is fast developing in our country, and analysis of aluminium and its various alloys is required for judging the quality of the products used both at home and abroad. Various indigenous laboratories employ different methods for analysing same constituents and, the results reported often vary considerably. This standard was first published in 1954 by Basic Non-ferrous Metals Sectional Committee, EDC 4, with a view to standardize the methods. As the years passed, a number of new alloys found use in the trade and some of these alloys contained elements for which the methods of analysis had not been prescribed in IS : 504-1954. Hence need was felt to revise the standard.

**0.3** Apart from some minor alterations, the changes as indicated in **0.3.1** to **0.3.3** have been made in this revision.

**0.3.1** To cover adequately the analysis of aluminium alloys, the following methods have been added:

Determination of:

- a) Silicon by the Molybdenum Yellow ( Photometric ) Method ( for Silicon Content between 0.02 to 0.3 percent ),
- b) Iron by the O-phenanthroline ( Photometric ) Method ( for Iron Content between 0.03 to 0.10 percent ),
- c) Copper by the Iodometric Method ( for Copper Content over 0.1 percent ),
- d) Zinc by the Dithizone ( Photometric ) Method ( for Zinc Content below 0.1 percent ),

- e) Zinc by the Mercuric Thiocyanate ( Volumetric ) Method ( for Zinc Content  $\leq 0.1$  percent ),
- f) Manganese by the Periodate ( Photometric ) Method ( for Manganese Content between 0.01 to 0.1 percent ),
- g) Manganese by the Bismuthate ( Alternate ) Method ( for Manganese Content between 0.1 to 1.5 percent ),
- h) Magnesium by Ethylenediamine Tetra-Acetate Method ( for Magnesium Content between 0.5 to 11 percent ),
- j) Tin by the Iodimetric Method, and
- k) Antimony by Potassium Iodide Thiourea ( Photometric ) Method.

**0.3.2** Colorimetric methods for the determination of copper and titanium have been replaced by the Photometric method.

**0.3.3** The following methods have been revised:

Determination of:

- a) Silicon by the Gravimetric Method,
- b) Lead by the Sulphide ( Colorimetric ) Method,
- c) Iron by the Titanous Chloride ( Volumetric ) Method,
- d) Zinc by the Mercuric Thiocyanate ( Gravimetric ) Method,
- e) Manganese by the Persulphate-Arsenite Method,
- f) Magnesium by the Oxine Method,
- g) Nickel by the Dimethylglyoxime ( Gravimetric ) Method, and
- h) Chromium by the Persulphate-Oxidation ( Volumetric ) Method.

**0.4** The methods of analysis prescribed in this standard have been prepared with a view that they shall be useful primarily as referee methods and could also be used by laboratories for their day-to-day work.

**0.5** While preparing this standard, the views of producers, consumers and testing authorities, relating to the technological methods followed in the country in this field were taken into account. Due weightage has also been given to the need for international co-ordination among standards prevailing in different countries of the world in this field.

1962 BOOK OF ASTM METHODS FOR CHEMICAL ANALYSIS OF METALS.  
American Society For Testing and Materials.

B.S. 558 & 564 : 1953 NICKEL ANODES AND NICKEL SALTS FOR ELECTRO-PLATING.

FURMAN, N.H. (Ed) SCOTT, W.W. Standard Methods of Chemical Analysis. 5th ed. New York. D. Van Nostrand Company. Inc. 1962.

HILLEBRAND, W.F., LUNDELL, G.E.F. AND BRIGHT, H.A. APPLIED INORGANIC ANALYSIS, 2nd ed. New York. John Willy & Sons, 1955.

**0.6** Wherever a reference to any Indian Standard appears in this standard, it shall be taken as a reference to the latest version of the standard.

**0.7** In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960 Rules for Rounding Off Numerical Values ( *Revised* ).

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## 1. SCOPE

**1.1** This standard prescribes the methods for determination of silicon, lead, iron, copper, zinc, manganese, magnesium, nickel, chromium, tin, antimony, and titanium in the ranges as prescribed in the relevant Indian Standard specifications on aluminium and its alloys.

**1.2** Different procedures have been recommended for different ranges of the same constituents. Also, modifications in the procedures have been recommended in case of those methods where interference due to certain elements is definite.

## 2. SAMPLING

**2.1** Samples shall be drawn and prepared in accordance with IS : 1817-1961 Methods of Sampling Non-ferrous Metals for Chemical Analysis.

## 3. GENERAL

**3.1 Use of Filter Papers** — In the methods prescribed in this standard, only relative numbers of Whatman filter papers, which are commonly used, have been given. However, any other suitable brand of filter paper of corresponding porosity may be used.

## 4. QUALITY OF REAGENTS

**4.1** Unless specified otherwise, pure chemicals and distilled water [ see\*IS: 1070-1960 Specification for water, Distilled Quality ( *Revised* ) ] shall be employed in the tests.

**NOTE** — ' Pure chemicals ' shall mean chemicals that do not contain impurities which affect the results of analysis.

\*Since revised.

## 5. DETERMINATION OF SILICON BY THE MOLYBDENUM YELLOW (PHOTOMETRIC) METHOD (FOR SILICON CONTENT BETWEEN 0.02 TO 0.3 PERCENT)

**5.1 Outline of the Method** — The sample is dissolved in sodium hydroxide and the solution acidified with nitric acid. The orthosilicic acid formed is converted to yellow silicomolybdic acid by the addition of ammonium molybdate to the solution. Photometric measurement of the yellow complex is then made at about 400 m $\mu$ .

### 5.2 Reagents

**5.2.1 Sodium Hydroxide Solution** — 40 percent (w/v). Weigh 40 g of sodium hydroxide pellets in a plastic, polythene or stainless steel beaker and add 100 ml of water. Stir with a plastic rod until entire mass dissolves. Cool and store in a plastic or polythene bottle.

**5.2.2 Dilute Nitric Acid** — 1 : 1 (v/v).

**5.2.3 Ammonium Molybdate Solution** — 10 percent (w/v). Dissolve 100 g of ammonium molybdate in water and dilute to one litre. Filter before use.

**5.2.4 Standard Silicon Solution** (1 ml = 0.05 mg of Si) — Fuse 0.1070 g of anhydrous silica with 1.0 g of sodium carbonate in a platinum crucible. Cool the melt, dissolve completely in water, and dilute to one litre in a volumetric flask. Store the solution in a polythene bottle. In case anhydrous silica is not available, adjust the weight of silica used according to the actual silicon content of the sample.

### 5.3 Procedure

**5.3.1** Transfer 0.5 g of the accurately weighed sample to a 250-ml stainless steel or nickel beaker. Add 10 ml of sodium hydroxide solution by means of a pipette. Cover the beaker and warm it to start the reaction. When the reaction subsides, wash the walls of the beaker and cover. Heat to complete the solution and boil for a few minutes. In case of alloys containing magnesium, concentrate the solution by boiling to ensure complete conversion of magnesium silicide to sodium silicate. Dilute the solution by washing the walls of the beaker and the cover with water. Cool and transfer the contents of the beaker to a Pyrex beaker containing 25 to 30 ml of dilute nitric acid (measured accurately). Transfer the contents of the metallic beaker completely to the glass beaker with a jet of water. Wash the metallic beaker three or four times with hot water, using a small quantity at a time, and transfer the washings to the glass beaker. Shake the contents of the beaker well and boil until the solution becomes clear (avoid excess boiling). Cool the solution.

**5.3.2** Filter the solution through filter paper No. 40 into a 250-ml volumetric flask. Wash the beaker 5 or 6 times with hot water. Dilute the solution to about 220 ml. Cool to room temperature, add 10 to 25 ml of ammonium molybdate solution and make up the volume to the mark. Shake the flask well. Allow the solution to stand for 15 minutes to develop the yellow colour fully.

**5.3.3** Transfer a suitable portion of the solution to an absorption cell (4 cm) and adjust the photometer to the initial setting. Take the photometric readings within ten minutes of the development of colour, using a light filter at approximately 400 m $\mu$ .

**5.3.4 Calibration Curve** — Take a series of standard silicon solutions and a reagent blank. Using same quantities of reagents, carry through all the stages as described under 5.3.2 and 5.3.3 and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of the standard solution against milligrams of silicon per 100 ml of the solution.

**5.4 Calculation** — Convert the photometric reading of the sample to milligrams of silicon by means of calibration curve, and calculate the percentage of silicon as follows:

$$\text{Silicon, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$  = weight in mg of silicon found in the aliquot solution, and

$B$  = weight in g of the sample represented by the aliquot taken.

**NOTE** — In case of high-manganese alloys, the solution after addition of nitric acid may be coloured brownish yellow. If so, bleach the colour by dropwise addition of saturated solution of sodium sulphite to the hot solution. Then add sufficient potassium permanganate solution (0.1 N) until a pink colour is obtained. Add finally just enough oxalic acid solution (one percent, w/v) to destroy the pink colour.

## 6. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD (FOR SILICON CONTENT OVER 0.3 PERCENT)

**6.1 Outline of the Method** — Silicon is converted to sodium silicate by alkaline attack. After acidification and removal of interfering elements, silica is determined by hydrofluorization of the residue.

### 6.2 Reagents

**6.2.1 Sodium Hydroxide Solution** — 50 percent (w/v).

**6.2.2 Hydrogen Peroxide** — 20 volumes.

**6.2.3 Concentrated Sulphuric Acid**—sp gr 1·84 [conforming to IS : 266-1961 Specification for Sulphuric Acid ( *Revised* ) ].

**6.2.4 Sulphuric Acid-Perchloric Acid Mixture**—Add 625 ml of concentrated sulphuric acid (sp gr 1·84) and 85 ml of perchloric acid (70 percent) to 315 ml of water.

**6.2.5 Perchloric Acid Solution**—Add 600 ml of perchloric acid (70 percent) to 400 ml of water.

**6.2.6 Concentrated Nitric Acid**—sp gr 1·42 (conforming to \*IS : 264-1950 Specification for Nitric Acid)

**6.2.7 Sulphurous Acid**—Saturate water with sulphur dioxide gas. Prepare fresh as needed.

**6.2.8 Dilute Sulphuric Acid**—1 : 1, 1 : 3 and 1 : 99 (v/v).

**6.2.9 Concentrated Hydrochloric Acid**—sp gr 1·16 [conforming to IS : 265-1952 Specification for Hydrochloric Acid ( *Revised* ) ].

**6.2.10 Ammonium Acetate Solution**—Dissolve 25 g of ammonium acetate in one millilitre of glacial acetic acid and 100 ml of water.

**6.2.11 Dilute Hydrochloric Acid**—1 : 99 (v/v).

**6.2.12 Hydrofluoric Acid**—40 percent.

### 6.3 Procedure

**6.3.1** Depending upon the silicon content of the sample, adjust the weight of the sample to be taken for analysis as given below. Accurately weigh the sample and transfer it to a stainless steel beaker or a nickel beaker :

<i>Silicon Content, Percent</i>	<i>Weight in g of the Sample to be Taken</i>
Over 0·3 up to 1	2
Over 1 up to 3	1
Over 3 up to 7	0·5
Over 7	0·25

**6.3.2** Add 12 ml of sodium hydroxide solution per gram of the sample taken. When the reaction is complete, wash down the cover and sides of the vessel with small jet of hot water. Keep the volume of the solution as low as possible. Place on the hot plate and evaporate cautiously to a syrupy consistency. Add hydrogen peroxide dropwise (about 30 drops) and repeat the evaporation. Add more hydrogen peroxide dropwise until the solution is completely oxidized. Remove the vessel from hot plate, cool, wash the sides with 10 ml of water, and pour into a

\*Since revised.

400-ml beaker containing 40 ml of sulphuric acid-perchloric acid mixture. Rinse the nickel vessel, first with hot water and then with a few millilitres of perchloric acid solution to which an equal volume of water has been added. Clean the vessel thoroughly by means of a rubber-tipped glass rod and finally rinse with hot water.

**6.3.3** Add 5 ml of concentrated nitric acid and a few millilitres of sulphuric acid to the solution, evaporate to dense white fumes, cover, fume for 15 minutes and cool. Add 100 ml of water and 10 ml of dilute sulphuric acid (1 : 3). Stir well and heat until the soluble salts are dissolved. If manganese dioxide is present, bring it into solution with a few drops of hydrogen peroxide or sulphurous acid.

**6.3.4** Add paper pulp, and filter on a low ash medium texture paper. Remove all silica from the beaker by means of rubber-tipped glass rod and wash the paper and contents thoroughly with dilute sulphuric acid (1 : 99). Recover silica from the filtrate by evaporating the filtrate, fuming and proceeding as under **6.3.3**. Add the recovered silica to the main silica residue. Place the papers and precipitate in a platinum crucible, dry and ignite slowly at 500°C until free of carbon; then heat at 900° to 950°C for 25 minutes. Cool in a desiccator, weigh and again ignite at the same temperature as a check for constant weight.

**6.3.5** If lead is present, wash the main silica residue (*see 6.3.4*) with hot ammonium acetate solution and preserve the ammonium acetate extract separately for determination of lead (*see 7*). Alternatively, the lead retained in the residue may be removed as under **6.3.5.1**.

**6.3.5.1** After fuming (*see 6.3.3*) take up the sample with 5 ml of concentrated hydrochloric acid and 100 ml of hot water. Filter and wash with hot dilute hydrochloric acid. The analyst may select the method for lead separation that best suits his plan for using the filtrate in subsequent analysis.

**6.3.6** Moisten the residue with a few drops of water, then add 5 to 10 drops of dilute sulphuric acid (1 : 1) and a few millilitres of hydrofluoric acid. Evaporate to dryness, ignite at 900°C, cool and weigh. Repeat the treatment with hydrofluoric acid and ignite to constant weight. The loss in weight represents silica.

**6.3.7** Make a blank determination, following the same procedure and using the same amounts of all reagents, but without the sample.

## 6.4 Calculation

$$\text{Total silicon, percent} = \frac{A - B}{C} \times 46.72$$

where

$A$  = weight in g of silica obtained in 6.3.6,

$B$  = weight in g of silica obtained in the blank, and

$C$  = weight in g of the sample taken.

## 7. DETERMINATION OF LEAD BY THE SULPHIDE (COLORIMETRIC) METHOD

**7.1 Outline of the Method** — Lead is determined colorimetrically from the ammonium acetate extract obtained from silicon determination.

### 7.2 Reagents

**7.2.1 Dilute Nitric Acid** — 1 : 1 (v/v).

**7.2.2 Sucrose Solution** — 100 percent (w/v).

**7.2.3 Hydrogen Sulphide Solution** — Saturate dilute sulphuric acid (1 : 99) with hydrogen sulphide gas.

**7.2.4 Standard Lead Solution** (1 ml = 0.0001 g of Pb) — Dissolve 0.1831 g of lead acetate crystals,  $[Pb(CH_3CO_2)_2 \cdot 3H_2O]$  in water containing a little acetic acid and dilute to one litre.

### 7.3 Procedure

**7.3.1** Transfer the ammonium acetate extract preserved under 6.3.5 to a 100-ml Nessler tube. Add water to make the solution to 90 ml. Add 3 drops of dilute nitric acid, one millilitre of sucrose solution and 5 ml of hydrogen sulphide solution. Make up the volume to 100 ml with water, and mix well. Compare the intensity of colour with those of series of standard solutions each containing same quantities of all the reagents as were added in the test solution. It is important to add hydrogen sulphide solution, simultaneously to the standard and test solutions.

### 7.4 Calculation

$$\text{Lead, percent} = \frac{A}{B} \times 0.1$$

where

$A$  = weight in mg of lead found in the sample, and

$B$  = weight in g of the sample taken.

## 8. DETERMINATION OF IRON BY THE O-PHENANTHROLINE (PHOTOMETRIC) METHOD (FOR IRON CONTENT BETWEEN 0.03 TO 0.10 PERCENT)

**8.1 Outline of the Method** — The sample is dissolved in sodium hydroxide solution and then acidified with hydrochloric acid. In an aliquot of the



solution, lead is added to replace copper and to reduce iron to ferrous state. O-phenanthroline, when added to the ferrous solution maintained at about pH 4, produces an orange-red complex. Photometric measurement is made at approximately 490 m $\mu$ .

## 8.2 Reagents

**8.2.1 Sodium Hydroxide Solution** — 20 percent (w/v).

**8.2.2 Lead, Low-Iron** — finely granulated lead containing under 0.001 percent of iron.

**8.2.3 Acetate Buffer Solution** — Dissolve 272 g of sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) in 500 ml of water. Add 240 ml of glacial acetic acid, cool and dilute to one litre.

**8.2.4 Hydroxylamine Hydrochloride Solution** — one percent (w/v).

**8.2.5 O-phenanthroline Solution** — 0.2 percent (w/v).

**8.2.6 Standard Iron Solution** (1 ml = 0.02 mg of Fe) — Dissolve 0.1405 g of ferrous ammonium sulphate [ $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ] in 100 ml of dilute hydrochloric acid (1 : 19) and dilute to one litre in a volumetric flask.

## 8.3 Procedure

**8.3.1** Transfer 0.5 g of the accurately weighed sample, from which adventitious iron has been removed by means of a magnet, to a nickel beaker and dissolve in 15 ml of sodium hydroxide solution, added in small increments. When the attack is complete, wash down the sides of the beaker, and boil gently until the silicon is completely dissolved. (For high-silicon alloys (silicon greater than 4 percent) heat the beaker to a temperature just below boiling point to oxidize the silicon.) Cool and transfer to a 250-ml glass beaker containing 25 ml of dilute hydrochloric acid (1 : 1). Boil until all salts are dissolved. Cool, filter through filter paper No. 4 into a 100-ml volumetric flask, dilute to the mark and mix.

**8.3.2** Transfer a suitable aliquot (containing 0.012 to 0.24 mg of iron to a 150-ml beaker, dilute to approximately 30 ml and add one to two grams of lead. Boil gently until all copper is displaced and iron reduced completely. Cool, transfer and wash by decantation to a 100-ml volumetric flask.

**8.3.3** Add 10 ml of sodium acetate-acetic acid buffer solution and 2 ml of hydroxylamine hydrochloride solution and mix. Add 10 ml of O-phenanthroline solution, dilute to the mark and mix.

**8.3.4** Transfer a suitable aliquot of the solution to a 2-cm absorption cell and adjust the photometer to the initial setting. Take the photometric reading using a light filter at 490 m $\mu$  approximately.

**8.3.5 Calibration Curve** — Take a series of standard iron solutions and the reagent blank. Using the same quantities of reagents, carry through all the stages as described under 8.3.3 and 8.3.4 and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve plotting the photometric readings of the standard solutions against milligrams of iron per 100 ml of the solution.

**8.4 Calculation** — Convert the photometric reading of the sample to milligrams of iron by means of calibration curve, and calculate the percentage of iron, as follows:

$$\text{Iron, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$  = weight in mg of iron found in the aliquot used, and

$B$  = weight in g of the sample represented by the aliquot taken.

## 9. DETERMINATION OF IRON BY THE TITANOUS CHLORIDE (VOLUMETRIC) METHOD (FOR IRON CONTENT BETWEEN 0.01 TO 2.0 PERCENT)

**9.1 Outline of the Method** — The sample is dissolved in mixed acids and fumed with sulphuric acid. The siliceous residue is filtered off and any traces of retained iron are recovered by subsequent treatment of the ignited residue. Copper is precipitated by hydrogen sulphide and the copper sulphide is filtered off. The hydrogen sulphide is removed from the filtrate by boiling, iron oxidized and then determined by titration with standard titanous chloride solution using potassium thiocyanate as indicator.

### 9.2 Reagents

**9.2.1 Concentrated Sulphuric Acid** — see 6.2.3.

**9.2.2 Concentrated Hydrachloric Acid** — see 6.2.9.

**9.2.3 Concentrated Nitric Acid** — see 6.2.6.

**9.2.4 Mixed Acids** — Add 170 ml of concentrated sulphuric acid cautiously, to 600 ml of water, cool and add 300 ml of concentrated hydrochloric acid and 300 ml of concentrated nitric acid.

**9.2.5 Dilute Sulphuric Acid** — 1 : 1 and 1 : 99 (v/v).

**9.2.6 Hydrofluoric Acid** — 40 percent.

**9.2.7 Potassium Bisulphate** — solid.

**9.2.8 Hydrogen Sulphide** — gas.

**9.2.9 Hydrogen Sulphide Wash Solution** — Saturate dilute sulphuric acid (1 : 99) with hydrogen sulphide gas.

**9.2.10 Potassium Permanganate Solutions** — 0.1 N and 0.02 N approx.

**9.2.11 Potassium Thiocyanate Solution** — 10 percent (w/v).

**9.2.12 Standard Titanous Chloride Solution** — Add about 100 ml of titanous chloride solution (150 g per litre) to 200 ml of concentrated hydrochloric acid, in a large beaker. Bring to the boil and boil for two minutes. Cool rapidly by diluting with cold water, and pour into a 5-litre aspirator already nearly filled with cold water (see Fig. 1). Add more water until the aspirator is practically overflowing and mix by shaking. Connect it to the side-arm burette and to the hydrogen generator, thus displacing a quantity of the solution. Remove all air from the tubes, and ensure that all spaces are filled with hydrogen. Allow the solution to stand overnight before it is standardized. Standardize as follows:

Transfer 0.3000 g of pure iron of known composition to a 250-ml beaker and dissolve in 30 ml of dilute hydrochloric acid (1 : 1). Oxidize with bromine water, adding a few drops in excess. Boil to expel the excess bromine. Add 25 ml of concentrated hydrochloric acid, cool and dilute to one litre in a volumetric flask. Pipette out 100-ml portion of this solution into a 250-ml beaker. Add 10 ml of potassium thiocyanate (10 percent) and titrate with the titanous chloride solution to complete loss of colour.

### 9.3 Procedure

**9.3.1** Transfer 2 to 5 g of the accurately weighed sample, after removal of any adventitious iron by means of a magnet, to a 500- to 800-ml conical beaker. Cover with a watch-glass and gradually add 70 to 175 ml of mixed acids as prescribed depending on the weight of the sample taken. Cool, if necessary, wash down the watch-glass and remove it. Evaporate the solution to fuming and fume for 10 minutes, cool to room temperature, add cautiously 100 to 150 ml of warm water and 5 ml of dilute sulphuric acid (1 : 1) and boil gently for 20 minutes to ensure complete solution of the salts. Filter through an ashless paper pulp pad containing some ashless paper pulp into a second 500-ml conical beaker. Wash the beaker and then wash the precipitate 6 to 8 times with hot dilute sulphuric acid (1 : 99). Preserve the filtrate.

**9.3.2** Ignite the siliceous precipitate in a platinum crucible at moderate temperature (less than 600°C if copper is being determined) until the

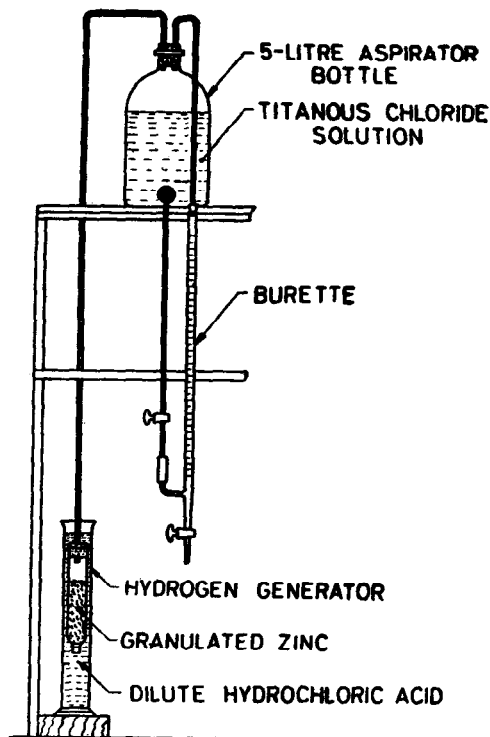


FIG. 1 APPARATUS FOR STORING TITANOUS CHLORIDE SOLUTION

carbon has completely disappeared. After cooling, treat the residue with 0.5 ml of concentrated sulphuric acid 2 to 3 ml of hydrofluoric acid and then add cautiously one millilitre of concentrated nitric acid, adding more hydrofluoric acid if necessary. Evaporate and re-ignite and add about 3 g of potassium bisulphate. Cover with a platinum lid and heat until the residue goes into solution. Cool and extract with warm dilute sulphuric acid into a 100-ml beaker. Boil the solution and then add to the preserved filtrate (*see 9.3.1*). Adjust the volume of the mixed solution to about 100 ml.

**9.3.3** Heat the combined filtrate to 60 to 70°C and pass a steady stream of hydrogen sulphide gas through the solution for 20 minutes. Add some ashless paper pulp and let stand for a few minutes to allow the precipitate to coagulate. Filter and wash the paper and precipitate 6 to 8 times with warm hydrogen sulphide wash solution (the precipitate may be used for copper determination) (*see 11.3.1*).

**9.3.4** Add 4 or 5 solid glass beads of a diameter of about 5 or 6 mm (to prevent bumping) and boil the filtrate vigorously for 25 to 30 minutes to remove hydrogen sulphide gas, or until the volume of the solution is reduced to half. Wash round the inside of the beaker and cool (*see Note*).

**NOTE** — A rough check for iron can be obtained by titration of some of the solution at this stage with potassium permanganate solution (0.02 N). In that case, titration should be done quickly in a cold solution.

**9.3.5** Oxidize the iron in the cold solution by dropwise addition of the potassium permanganate solution until the solution is just pink. Add at once 10 ml of potassium thiocyanate solution and titrate with the standard titanous chloride solution to a complete loss of red colour.

**9.3.6** Carry out a blank determination following the same procedure and using the same amounts of all reagents, but without the sample.

## 9.4 Calculation

$$\text{Iron, percent} = \frac{(A - B) C}{D} \times 100$$

where

*A* = volume in ml of titanous chloride solution required to titrate the sample,

*B* = volume in ml of titanous chloride solution required to titrate the blank,

*C* = iron equivalent of the titanous chloride solution in g per ml, and

*D* = weight in g of the sample taken.

## 10. DETERMINATION OF COPPER BY THE DIETHYL-DITHIO-CARBAMATE (PHOTOMETRIC) METHOD (FOR COPPER CONTENT BELOW 0.1 PERCENT)

**10.1 Outline of the Method** — The sample is treated with mixed acids and silicon removed. Copper is precipitated as sulphide from the acid solution of the sample and any copper left in the residue is also recovered. The copper is dissolved in nitric acid, complexed with diethyl-dithiocarbamate and determined photometrically at approximately 436 mμ.

### 10.2 Reagents

**10.2.1 Mixed Acids** — *see 9.2.4.*

**10.2.2 Dilute Sulphuric Acid** — 1 : 1, 1 : 99 (v/v).

**10.2.3 Hydrofluoric Acid** — 40 percent.

**10.2.4 Hydrogen Sulphide** — gas.

**10.2.5 Hydrogen Sulphide Wash Solution** — Pass hydrogen sulphide gas through dilute sulphuric acid (1 : 99).

**10.2.6 Dilute Nitric Acid** — 1 : 2 (v/v).

**10.2.7 Concentrated Ammonium Hydroxide** — 20 percent.

**10.2.8 Dilute Ammonium Hydroxide Wash Solution** — 1 : 20 (v/v).

**10.2.9 Citric Acid Solution** — 20 percent (w/v).

**10.2.10 Sodium Diethyl-Dithiocarbamate Solution** — 0.1 percent (w/v).

**10.2.11 Carbon Tetrachloride**

**10.2.12 Sodium Sulphate** — solid.

**10.2.13 Standard Copper Solution** (1 ml = 0.01 mg of Cu) — Dissolve one gram of electrolytic copper in 10 ml of dilute nitric acid (1 : 1), evaporate nearly to dryness and dilute to 1000 ml in a volumetric flask. Pipette 10 ml from this solution and dilute to one litre.

### 10.3 Procedure

**10.3.1** Transfer 2 g of the accurately weighed sample to a 400-ml beaker. Add 10 ml of the mixed acids and after the reaction has subsided, add 60 ml more. Add 20 ml of dilute sulphuric acid (1 : 1) and evaporate the solution to fumes. Continue fuming for ten minutes. Cool, dilute to 200 ml and boil until soluble salts are dissolved; filter the insoluble matter on a paper pulp pad and wash with hot dilute sulphuric acid (1 : 99). Preserve the filtrate.

**10.3.2** Ignite the residue in a silica basin at a temperature not exceeding 600°C. Transfer the residue to a platinum crucible. Moisten it with a little water. Add two to three drops of dilute sulphuric acid (1 : 1) and 8 to 10 ml of hydrofluoric acid. Evaporate to dryness and ignite for about five minutes, dissolve in a few millilitres of water and mix with the filtrate preserved under 10.3.1.

**10.3.3** Adjust the volume to 300 ml. Heat the solution to 60°C, add a small quantity of ashless paper pulp and pass hydrogen sulphide for about half an hour and keep for another half an hour at about 50 to 60°C. Filter through filter paper No. 41 and wash 8 to 10 times with hydrogen sulphide wash solution. Transfer the filter paper along with the precipitate to the same beaker in which copper was precipitated. Add 30 to 40 ml of dilute nitric acid (1 : 2) and digest on a hot plate for 15 to 20 minutes. Dilute to 70 to 80 ml with hot water and make distinctly ammoniacal. Keep just boiling for 3 to 4 minutes and filter through

filter paper No. 40 into a 200-ml volumetric flask. Wash with hot dilute ammonium hydroxide wash solution and discard the residue.

**10.3.4** Pipette a suitable aliquot ( depending on the copper content of the solution ) into a 250-ml separating funnel. Add 10 ml of citric acid. Make distinctly ammoniacal. Add 10 ml of sodium diethyl-dithiocarbamate solution mix well and allow to stand for 15 minutes. Extract successively with 25 ml, 15 ml and 10 ml of carbon tetrachloride. Combine carbon tetrachloride extracts and make up to 50 ml in a graduated flask. Add a little anhydrous sodium sulphate to clear the solution.

**10.3.5** Transfer a suitable aliquot to an absorption cell and adjust the photometer to the initial setting. Take the photometric reading using a light filter at approximately 435 m $\mu$ .

**10.3.6 Calibration Curve** — Take a series of standard copper solutions and a reagent blank. Using same quantities of all reagents, carry through all the stages as described under 10.3.4 and 10.3.5 and record the photometric readings of the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of standard solutions against milligrams of copper per hundred ml of the solution.

**10.4 Calculation** — Convert the photometric readings of the sample to milligrams of copper by means of calibration curve, and calculate to the percentage of copper as follows:

$$\text{Copper, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$  = weight in mg of copper found in the aliquot solution, and

$B$  = weight in g of the sample represented by the aliquot taken.

NOTE — Since the carbon tetrachloride extract of copper complex is readily bleached by exposure to strong light, extraction should, therefore, be carried out in artificial light or weak daylight.

## 11. DETERMINATION OF COPPER BY THE IODOMETRIC METHOD (FOR COPPER CONTENT OVER 0.1 PERCENT)

**11.1 Outline of the Method** — The sample is treated with mixed acids, the silicon removed by fuming and subsequent filtration and copper in the filtrate is precipitated as sulphide. The copper sulphide is ignited and dissolved in acid and the copper determined iodometrically. Antimony, if present, is separated from the copper sulphide in alkaline sulphide solution.

## 11.2 Reagents

**11.2.1 Concentrated Sulphuric Acid** — see 6.2.3.

**11.2.2 Concentrated Nitric Acid** — see 6.2.6.

**11.2.3 Concentrated Hydrochloric Acid** — see 6.2.9.

**11.2.4 Mixed Acids** — To 700 ml of water add gradually 150 ml of concentrated sulphuric acid. Cool, then add 75 ml of concentrated nitric acid and 75 ml of concentrated hydrochloric acid.

**11.2.5 Hydrofluoric Acid** — 40 percent.

**11.2.6 Dilute Sulphuric Acid** — 1:1 (v/v).

**11.2.7 Ammonium Fluoride** — solid.

**11.2.8 Concentrated Ammonium Hydroxide** — 20 percent.

**11.2.9 Acetic Acid** — glacial.

**11.2.10 Urea Solution** — 20 percent (w/v). Dissolve 20 g of urea in 100 ml of distilled water.

**11.2.11 Potassium Iodide Solution** — 50 percent (w/v).

**11.2.12 Standard Sodium Thiosulphate Solution** — 0.05 N and 0.02 N. Dissolve 12.41 g of sodium thiosulphate in distilled water and make up to 1 000 ml. Stabilize by the addition of two to three grams of borax per litre. For preparing standard thiosulphate solution (0.02 N), dilute 200 ml of standard thiosulphate solution (0.05 N) to 500 ml with water. This solution shall be used when the copper content is between 0.3 to 2.5 percent. Standardize the solution as described under 11.2.12.1.

**11.2.12.1** Weigh out exactly one gram of electrolytic copper, dissolve in 10 ml of dilute nitric acid (1:1). Boil nearly to dryness and dilute with water. Cool and make up the solution to 250 ml in a graduated flask. Pipette out exactly 25 ml (for standardizing 0.05 N thiosulphate solution) or 10 ml (for standardizing 0.02 N solution). Add ammonium fluoride, ammonia, acetic acid and urea as described under 11.3 and titrate with thiosulphate solution to be standardized, using starch as indicator.

**11.2.13 Starch Solution** — Make a suspension of one gram of soluble starch in about 10 ml of water and add it carefully to 100 ml of boiling water. Boil for two to three minutes and cool. Prepare the solution fresh as needed.

**11.2.14 Ammonium Thiocyanate** — solid.



**11.2.15 Hydrochloric Acid-Nitric Acid Mixture** — Mix 500 ml of concentrated hydrochloric acid (see 6.2.9) with 500 ml of concentrated nitric acid (see 6.2.6).

**11.2.16 Sodium Hydroxide Solution** — 20 percent (w/v).

**11.2.17 Sodium Sulphide Solution** — 15 percent (w/v).

**11.2.18 Sodium Hydroxide-Sodium Sulphide Wash Solution** — Mix equal volumes of sodium hydroxide solution (one percent) and sodium sulphide solution (one percent).

**11.2.19 Dilute Nitric Acid** — 1:1 (v/v).

**11.2.20 Sulphurous Acid** — Saturate water with sulphur dioxide. Prepare fresh as needed.

**11.2.21 Hydrogen Sulphide** — gas.

**11.2.22 Hydrogen Sulphide Wash Solution** — Saturate dilute sulphuric acid (1:99) with hydrogen sulphide gas.

### 11.3 Procedure (In the Absence of Antimony)

**11.3.1** Take 2 g of the accurately weighed sample (see Note) in a 400-ml beaker and treat with 50 ml of mixed acids. After the reaction has subsided, add 20 ml more of the mixed acids, adding a little concentrated nitric acid, if necessary. If silicon content is small (less than 2 percent), the recovery of copper from the residue is unnecessary provided that sufficient hydrofluoric acid is added at this stage to give a clear solution. Add 20 ml of dilute sulphuric acid, evaporate the solution to fuming and continue fuming for 10 minutes, cool, dilute to 200 ml and boil until the solution is clear. Filter off the insoluble matter on a paper pulp pad and wash with hot water. Precipitate copper by following the procedure exactly as described under 9.3.3.

NOTE — The precipitate of copper sulphide obtained under 9.3.2 may be employed directly, depending upon the composition of the alloy.

**11.3.2** Dry and ignite the copper sulphide residue at not more than 700°C in a porcelain or silica crucible. Moisten the residue in the crucible with a few drops of water and warm with 2 to 3 ml of concentrated nitric acid to dissolve. Transfer to 300-ml conical flask or beaker, boil nearly to dryness to remove most of the excess nitric acid and re-dissolve in approximately 10 ml of water.

**11.3.3** Add 0.1 to 0.2 g of ammonium fluoride, neutralize carefully by adding concentrated ammonium hydroxide drop by drop until blue complex is formed, and then add one drop in excess. Acidify with glacial acetic acid added dropwise, and add ten drops in excess, followed by a drop of urea solution. Wash the sides of the flask or beaker using

not more than 5 ml of water. Add 5 ml of potassium iodide solution and titrate with standard sodium thiosulphate solution adding one millilitre starch solution as indicator towards the end of the titration. Add about one to two grams of ammonium thiocyanate (to liberate the absorbed iodine) and continue the titration until the blue colour is completely discharged.

### 11.3.4 Calculation

$$\text{Copper, percent} = \frac{A \times B}{C} \times 100$$

where

$A$  = volume in ml of the standard sodium thiosulphate solution required to titrate the sample,

$B$  = copper equivalent of the standard sodium thiosulphate solution in g/ml, and

$C$  = weight in g of the sample taken.

## 11.4 Procedure ( In the Presence of Antimony and Tin )

**11.4.1** Treat 2 g of the accurately weighed sample in a 600-ml beaker with 40-ml of hydrochloric acid-nitric acid mixture. When the reaction is complete, dilute slightly and evaporate by boiling until just pasty. Dissolve in a small amount of water and pour into 100 ml of sodium hydroxide solution with constant stirring. Dilute to 300 ml, bring to the boil, add 25 ml of sodium sulphide solution, re-boil and allow the precipitate to settle for 30 minutes. Filter on a paper pulp pad and wash with sodium hydroxide-sodium sulphide wash solution.

**11.4.2** Extract the residue with hot dilute nitric acid adding a little sulphurous acid, if necessary, and wash with hot water. Add 5 ml of concentrated sulphuric acid and evaporate by boiling to a low bulk. Dry the paper pulp pad, from which the bulk of the copper sulphide has been extracted, and ignite for 20 to 30 minutes in a platinum crucible at approximately 700°C. Dissolve the residue in a few drops of concentrated nitric acid, add a few drops of hydrofluoric acid, if necessary, to remove the silicon, combine with the sulphuric acid solution obtained above and evaporate the solution to fuming, cool, dilute with 250 ml of hot water, heat to 60°C and saturate with hydrogen sulphide gas. Filter off the copper sulphide and wash with hydrogen sulphide wash solution, dry and ignite the paper and the residue as before. Moisten the residue in the crucible with a few drops of water and warm with 2 to 3 ml of concentrated nitric acid to dissolve. Transfer to a conical flask or beaker, boil nearly to dryness and dissolve in a small amount of water. Proceed further as described under 11.3.3 and 11.3.4.

## 12. DETERMINATION OF ZINC BY THE DITHIZONE (PHOTOMETRIC) METHOD (FOR ZINC CONTENT BELOW 0.1 PERCENT)

**12.1 Outline of the Method** — The sample is dissolved in hydrochloric acid and potassium chlorate. Red colour complex obtained by the addition of dithizone to an aliquot of the solution is extracted with carbon tetrachloride and determined photometrically at about 530 m $\mu$ .

### 12.2 Reagents

**12.2.1 Dilute Hydrochloric Acid** — 1 : 1 (v/v).

**12.2.2 Potassium Chlorate** — solid.

**12.2.3 Carbon Tetrachloride**

**12.2.4 Complex-Forming Solution** — Add successively, with shaking, to a 500-ml separatory funnel, 15 drops of concentrated ammonium hydroxide, 1.5 ml of ammonium oxalate solution (5 percent), 15 ml of sodium acetate (5 percent), 35 ml of hydrochloric acid (1 N), 85 ml of sodium acetate (5 percent) and a mixture of 120 ml of sodium thiosulphate solution (50 percent) and 150 ml of sodium sulphide solution (one percent). Shake the solution with small portions of dithizone until the latter remains green. Since the extraction of zinc proceeds slowly, it is better to use a shaking machine and allow 10 minutes for the reaction. Remove droplets of dithizone by finally washing with carbon tetrachloride. Slight separation of sulphur in aqueous solution does no harm.

**12.2.5 Dithizone Solution** — Dissolve 0.01 g of the reagent in 100 ml of carbon tetrachloride.

**12.2.6 Sodium Sulphide Wash Solution** — Dissolve 5 g of sodium sulphide in 500 ml of water. Dilute 25 ml of the solution to 500 ml.

**12.2.7 Standard Zinc Solution (1 ml 0.1 = mg of Zn)** — Dissolve 0.1 g of pure zinc in 5 to 10 ml of dilute hydrochloric acid (1 : 1). Cool and dilute to one litre in a volumetric flask. Transfer 10 ml of this solution to a 100-ml volumetric flask and make up the volume to the mark.

### 12.3 Procedure

**12.3.1** Dissolve 0.25 g of the accurately weighed sample in 12.5 ml of dilute hydrochloric acid, add 0.2 g of potassium chlorate and boil for five minutes. Dilute the solution to 250 ml in the volumetric flask and filter through coarse paper, rejecting the first portion of the filtrate.

**12.3.2** Pipette a suitable aliquot ( depending upon the zinc content of the sample ) into a 100-ml separatory funnel, add 30 ml of complex-forming solution and 10 ml of dithizone solution and shake vigorously. If the carbon tetrachloride becomes red or red-violet in a short time, draw off the extract into a graduated glass stoppered, 25-ml cylinder and shake with a 5 ml portion of dithizone solution. If after 5 minutes the carbon tetrachloride is only a dark violet, separate it, add one ml of dithizone solution and shake for a minute. The last extract shall remain green. Wash the last extract with carbon tetrachloride.

**12.3.3** Add 5 ml of the sodium sulphide wash solution to the combined extract and dilute the latter to 25 ml with carbon tetrachloride. Shake a few times with the wash solution and draw off the carbon tetrachloride phase. Repeat the washings three to four times with 5 ml portions of the wash solution. The last portion of the wash solution shall remain colourless. Filter the carbon tetrachloride extract through an acid-free filter paper of coarse texture to remove water droplets. Transfer a suitable portion of the solution to an absorption cell and take the photometric readings using a light filter at 530 m $\mu$ .

**12.3.4 Calibration Curve** — Take a series of standard zinc solutions and the reagent blank. Using the same quantities of reagents, carry through all stages as described under 12.3.2 and 12.3.3 and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of standard solutions against milligrams of zinc per hundred millilitres of the solution.

**12.4 Calculation** — Convert the photometric reading of the sample to milligrams of zinc by means of calibration curve, and calculate the percentage of zinc as follows:

$$\text{Zinc, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$  = weight in mg of zinc found in the aliquot of the sample solution used; and

$B$  = weight in g of the sample represented by the aliquot taken.

## 13. DETERMINATION OF ZINC BY MERCURIC THIOCYANATE METHOD

**13.1 Outline of the Method** — The sample is dissolved in mixed acids, silicon and copper precipitated by fuming and by means of hydrogen sulphide respectively. From the filtrate zinc is precipitated as sulphide in the presence of formic acid. Zinc sulphide is extracted with acid and

zinc mercuric thiocyanate precipitated from the extract, dried and weighed or titrated with standard potassium iodate solution depending upon the zinc content.

## 13.2 Reagents

**13.2.1 Mixed Acid** — Add 150 ml of concentrated sulphuric acid (see 6.2.3) cautiously to 700 ml of water and cool. Then add 75 ml of concentrated hydrochloric acid (see 6.2.9) and 75 ml of concentrated nitric acid (see 6.2.6).

**13.2.2 Dilute Sulphuric Acid** — 1 : 1 (v/v).

**13.2.3 Hydrogen Sulphide** — gas.

**13.2.4 Hydrogen Sulphide Wash Solution** — Saturate sulphuric acid (one percent) with hydrogen sulphide gas.

**13.2.5 Tartaric Acid Solution** — 30 percent (w/v).

**13.2.6 Concentrated Ammonium Hydroxide** — 20 percent.

**13.2.7 Methyl Red Indicator Solution** — 0.1 percent (w/v). Dissolve 0.1 g of methyl red in 3.72 ml of sodium hydroxide solution (0.1 N) and dilute to 250 ml with water. Filter, if necessary.

**13.2.8 Formic Acid Mixture** — To 20 ml of formic acid (sp gr 1.20), add 25 g of ammonium sulphate and 3 ml of concentrated ammonium hydroxide and dilute to 100 ml.

**13.2.9 Formic Acid Wash Solution** — Dilute 25 ml of formic acid mixture to one litre and saturate with hydrogen sulphide gas.

**13.2.10 Dilute Hydrochloric Acid** — 1 : 1 (v/v).

**13.2.11 Concentrated Nitric Acid** — see 6.2.6.

**13.2.12 Ammonium Nitrate** — solid.

**13.2.13 Methylated Spirit** — industrial.

**13.2.14 Sulphuric Acid-Industrial Methylated Spirit Mixture** — Add one millilitre of concentrated sulphuric acid to 200 ml of water and then add 200 ml of industrial methylated spirit.

**13.2.15 Mercuric Potassium Thiocyanate Solution** — Dissolve 54 g of mercuric chloride in water, add to 76 g of potassium thiocyanate dissolved in water and dilute to two litres. Filter before use.

**13.2.16 Concentrated Hydrochloric Acid** — see 6.2.9.

**13.2.17 Chloroform**

**13.2.18 Standard Zinc Solution** ( $1\text{ ml} = 0.0001\text{ of Zn}$ ) — Dissolve 0.1 g of pure electrolytic zinc in sufficient dilute sulphuric acid (1 : 1) and dilute to 1 000 ml with water.

**13.2.19 Standard Potassium Iodate Solution** — Dissolve 9.820 g of potassium iodate in water and dilute to, 1 000 ml. Pipette three portions each of 20 ml of standard zinc solution into separate 200-ml beakers. To each add 5 ml of dilute sulphuric acid (1 : 1), dilute to 75 ml with water and precipitate with 25 ml of mercuric potassium thiocyanate solution. Filter, wash the precipitates. Extract and titrate each extract separately with standard potassium iodate solution as described in the procedure. From the mean titre adjust the strength of the potassium iodate solution so that  $1\text{ ml} = 0.0001\text{ g}$ ,  $0.0002\text{ g}$  or  $0.0005\text{ g}$  of zinc depending on the amount of zinc expected in the sample.

### 13.3 Procedure [Gravimetric Method (for Zinc Content over 0.1 Percent)]

**13.3.1** Depending upon the zinc content of the sample, adjust the weight of the sample and volume of the mixed acid as given below to a conical weighed beaker:

Zinc Content, Percent	Weight in g of the Sample to be Taken	Volume in ml of the Mixed Acid Required
Over 2 up to 4	0.5	25
Over 1 up to 2	1	35
Over 0.1 up to 1	2	70
Over 0.05 up to 0.1	3	90
Upto 0.05	5	100

**13.3.2** Cool, if necessary. Add 20 ml of dilute sulphuric acid carefully, evaporate to fumes and continue fuming for 10 minutes; cool, dilute to 200 ml with water and boil until solution is complete. Cool to about 60 to 70°C and pass hydrogen sulphide rapidly through the solution for approximately 20 minutes. Allow the precipitate to coagulate. Immediately filter the silica and copper sulphides on a paper pulp pad, wash with warm hydrogen sulphide wash solution.

**13.3.3** Boil the filtrate to remove all hydrogen sulphide gas and adjust the volume to about 250 ml. Add 25 ml of tartaric acid solution and neutralize with concentrated ammonium hydroxide using methyl red as indicator. Add 25 ml of formic acid mixture, heat to 70 to 80°C. Add a little paper pulp and pass hydrogen sulphide gas rapidly through the solution for 30 minutes. Allow the precipitate of zinc sulphide to coagulate, filter on a pulp pad and wash with warm formic acid wash solution. Extract the precipitate with dilute hydrochloric acid and wash with hot water. Add 5 ml of concentrated nitric

acid and 10 ml of dilute sulphuric acid. Evaporate to fuming, decolourize with a few crystals of ammonium nitrate and fume for 10 minutes. Wash down and re-fume for 10 minutes, cool, dilute to 50 ml with water, add 50 ml of methylated spirit, mix well and allow to stand overnight. Filter the lead sulphate through a sintered-glass filtered funnel containing paper pulp pad using gentle suction, and wash with cold sulphuric acid-industrial methylated spirit mixture.

**13.3.4** Evaporate the filtrate to dryness, add 35 ml of water and 10 ml of dilute sulphuric acid, boil until clear. Cool and precipitate the zinc with 25 ml of mercuric potassium thiocyanate solution with vigorous stirring. Allow to stand for at least eight hours and filter by suction on a weighed sintered-glass crucible. Wash six times (25 ml each time) with mercuric potassium thiocyanate solution, diluted 50 times. Dry at 110°C to constant weight.

**13.3.5** Carry out a blank determination, following the same procedure and using the same amounts of all reagents, but without the sample.

### 13.3.6 Calculation

$$\text{Zinc, percent} = \frac{(A - B)}{C} \times 13.12$$

where

*A* = weight in g of zinc mercuric thiocyanate,

*B* = correction for the blank in g, and

*C* = weight in g of the sample taken.

## 13.4 Procedure [By Mercuric Thiocyanate (Volumetric) Method (for Zinc Content ≤ 0.1 Percent)]

**13.4.1** Take the filtered and washed zinc mercuric thiocyanate precipitate as obtained under 13.3.4 in a 60-ml wide mouthed bottle. From a pipette add dropwise 2 ml of concentrated hydrochloric acid round the edge of the sintered-glass filter funnel. Allow to stand for one minute and then apply suction. Add further 2 ml of concentrated hydrochloric acid dropwise as before, wash alternately with one millilitre of water and concentrated hydrochloric acid. Finally pour 0.5 ml of water. Add 0.5 to one ml of chloroform to the solution in the bottle and titrate with standard potassium iodate solution until the chloroform layer is just colourless. In most cases the titration is started by adding 4 drops of the iodate solution and then shaking. Further additions are then made drop by drop with thorough shaking.

### 13.4.2 Calculation

$$\text{Zinc, percent} = \frac{(A - B) C}{D} \times 100$$

where

*A* = volume in ml of the standard potassium iodate solution used in the test,

*B* = volume in ml of the standard potassium iodate solution required for the blank,

*C* = zinc equivalent of the standard potassium iodate solution in g/ml, and

*D* = weight in g of the sample taken.

#### 14. DETERMINATION OF MANGANESE BY THE PERIODATE (PHOTOMETRIC) METHOD (FOR MANGANESE CONTENT BETWEEN 0.01 TO 0.1 PERCENT)

**14.1 Outline of the Method**—Manganese in the solution of the sample is oxidized to permanganate by means of potassium periodate. The absorption of the solution is measured at about 525 m $\mu$ . The permanganate is reduced by nitrite and the absorption of the reduced solution is deducted.

##### 14.2 Reagent

**14.2.1 Sodium Hydroxide Solution**—15 percent (w/v).

**14.2.2 Sodium Nitrite Solution**—2 percent (w/v).

**14.2.3 Acid Mixture**—Mix 325 ml of concentrated nitric acid (see 6.2.6) and 25 ml of the syrupy phosphoric acid (85 percent) with 150 ml of water.

**14.2.4 Hydrofluoric Acid**—40 percent.

**14.2.5 Potassium Periodate Solution**—Cautiously add 25 ml of concentrated sulphuric acid (see 6.2.3) to 50 ml of water. Cool and dilute to 100 ml. Dissolve 7.5 g of potassium periodate in this solution.

**14.2.6 Standard Manganese (Stock) Solution (1 ml = 0.25 mg of Mn)**—Dissolve a weighed quantity of electrolytic pure manganese of known manganese content in 5 ml of dilute nitric acid (1:1) the quantity weighed being such as will give 0.2500 g of manganese; cool and dilute to one litre.

**14.2.6.1 Standard manganese solution**—Dilute part of the solution prepared under 14.2.5, so that 1 ml = 0.05 mg of manganese.

##### 14.3 Procedure

**14.3.1** Treat 0.5 g of the accurately weighed sample in a 250-ml beaker with 25 ml of the sodium hydroxide solution. Cover with a watch-glass



and when the reaction slows down, boil gently for not more than 5 minutes. If any manganese dioxide forms, reduce it by dropwise addition of the sodium nitrite solution, avoiding any unnecessary excess. Wash down the watch glass with not more than 5 ml of water. Cool slightly and add 25 ml of the acid mixture while shaking vigorously. Boil for at least 3 minutes to expel nitrous fumes. Filter off silica and recover manganese from silica after volatilization of the residue with hydrofluoric acid.

**14.3.2** Add 3 ml of the potassium periodate solution and cover with watch-glass again. Boil gently until the colour starts to develop and continue boiling for about 3 minutes. Keep hot (for example, on edge of a hot plate) but not boiling for a further 3 to 5 minutes, add about 25 ml of cold water (to prevent salts from crystallization during cooling), cool, transfer to a 100-ml volumetric flask and dilute to the mark.

**14.3.3** Transfer a suitable aliquot to an absorption cell and adjust the photometer to the initial setting. Take the photometric readings using a light filter at approximately 525 m $\mu$ .

**14.3.4 Calibration Curve** — Take a series of standard manganese solutions and the reagent blank. Using same quantities of all reagents, carry through all the stages as described under **14.3.2** and **14.3.3** and record the photometric readings of all the standard solutions along with the blank. Draw a calibration curve by plotting the photometric readings of standard solutions against milligrams of manganese per hundred millilitres of the solution.

**14.4 Calculation** — Convert the photometric readings of the sample to milligrams of manganese by means of calibration curve, and calculate the percentage of manganese as follows:

$$\text{Manganese, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

*A* = weight in mg of manganese found in the aliquot solution, and

*B* = weight in g of the sample represented by the aliquot taken.

## 15. DETERMINATION OF MANGANESE BY THE PERSULPHATE ARSENITE METHOD (FOR CHROMIUM CONTENT UP TO 0.5 PERCENT)

**15.1 Outline of the Method** — Manganese in the solution of the sample is oxidized to permanganic acid by means of potassium persulphate in presence of silver nitrate. The permanganic acid is then titrated with standard arsenite nitrite mixture.

**15.2 Reagents**

**15.2.1 Sodium Hydroxide Solution** — 20 percent (w/v).

**15.2.2 Acid Mixture** — Add 250 ml of concentrated sulphuric acid (see 6.2.3) cautiously to 1 550 ml of water, cool, and add 500 ml of phosphoric acid (85 percent) and 200 ml of concentrated nitric acid (see 6.2.6).

**15.2.3 Silver Nitrate Solution** — 0.12 percent (w/v). Prepare fresh as needed.

**15.2.4 Ammonium Persulphate Solution** — 25 percent (w/v).

**15.2.5 Ammonium Chloride Solution** — 0.15 percent (w/v).

**15.2.6 Standard Arsenite-Nitrite Mixture (0.05 N Approximately)** — Mix 660 ml of the sodium arsenite solution (see 15.2.6.1) with 340 ml of the sodium nitrite solution (see 15.2.6.2). Dissolve one gram of manganese-free pure aluminium in 25 ml of sodium hydroxide solution, add 10 ml of the standard manganese solution prepared under 15.2.6.3 and acidify with 60 ml of the acid mixture. Continue as described under procedure. Carry out the standardization in triplicate and from the mean of the results calculate the strength of the arsenite-nitrite mixture in terms of manganese. This standardization should be carried out with each batch of the determination.

**15.2.6.1 Sodium arsenite (0.05 N Approximately)** — Dissolve 2.47 g of arsenous oxide in 25 ml of warm water containing 1.5 g of sodium hydroxide. Add 4 g of sodium hydrogen carbonate, cool and dilute to one litre.

**15.2.6.2 Sodium nitrite (0.05 N approximately)** — Dissolve 1.72 g of sodium nitrite (previously dried at 105° to 110°C for one hour) in water and dilute to one litre.

**15.2.6.3 Standard manganese solution** — Dissolve a weighed quantity of electrolytic pure manganese of known manganese content in 10 ml of dilute nitric acid (1:1), the quantity weighed being such as will give 0.500 0 g of manganese, cool and dilute to one litre.

**15.3 Procedure**

**15.3.1** Depending upon the manganese content of the sample, transfer an accurately weighed sample as given below to a 500-ml conical beaker (with a 230-ml mark):

<i>Manganese Content, Percent</i>	<i>Weight in g of the Sample to be Taken</i>
Over 1.0 up to 1.5	0.5
Over 0.25 up to 1.0	1
Over 0.1 up to 0.25	2

**15.3.2** Treat the sample with 25 ml of sodium hydroxide solution (50 ml for a 2 g sample) and bring to boiling point on a hot plate until all visible action ceases. (For silicon content greater than 4 percent, concentrate the solution at this stage to about half volume). Cool slightly, then add 60 ml of the acid mixture (100 ml for a 2 g sample) wash down the sides of the beaker and boil gently until solution is complete and nitrous fumes are expelled.

**15.3.3** Add a few particles of crushed silica to prevent bumping, dilute to the 230-ml mark with hot water and add 10 ml of silver nitrate solution and 10 ml of ammonium persulphate solution. Heat to boiling point and boil gently for one minute after the initial formation of permanganic acid. Cool to  $20 \pm 3^\circ\text{C}$  and add 10 ml of ammonium chloride solution to precipitate silver. Titrate with standard arsenite-nitrite mixture until permanganic acid is completely reduced and addition of one drop produces no further change in colour.

NOTE—The titration should be carried out rapidly as otherwise part of manganese may be reoxidized by ammonium persulphate during the titration, yielding high results.

## 15.4 Calculation

$$\text{Manganese, percent} = \frac{A \times B}{C} \times 100$$

where

$A$  = volume in ml of standard arsenite-nitrite mixture used in the test,

$B$  = manganese equivalent of the standard arsenite solution in g/ml, and

$C$  = weight in g of the sample taken.

## 16. DETERMINATION OF MANGANESE BY THE BISMUTHATE (ALTERNATE) METHOD (FOR MANGANESE CONTENT BETWEEN 0.1 TO 1.5 PERCENT)

**16.1 Outline of the Method**—Manganese in the solution of the sample is oxidized to permanganic acid by means of sodium bismuthate in nitric acid medium and the permanganate thus formed is titrated with standard ferrous ammonium sulphate solution.

### 16.2 Reagents

**16.2.1 Concentrated Nitric Acid**—see 6.2.6.

**16.2.2 Sodium Bismuthate**—solid.

**16.2.3 Sulphurous Acid** — Make approximately 5 percent solution of sulphur dioxide in water.

**16.2.4 Dilute Nitric Acid** — 3:97 (v/v).

**16.2.5 Phosphoric Acid** — 85 percent (w/v).

**16.2.6 Standard Ferrous Ammonium Sulphate Solution** — 0.03 N. Dissolve 6 g of ferrous ammonium sulphate [ $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ] in cold dilute sulphuric acid (5:95) add make the volume to 500 ml with this acid. Mix well and keep in an amber-coloured glass-stoppered bottle.

**16.2.7 Standard Sodium Oxalate Solution** — 0.03 N. Dissolve 2.01 g of sodium oxalate in water and make up to one litre in a graduated flask.

**16.2.8 Standard Potassium Permanganate Solution** — 0.03 N. Dissolve 0.958 g of potassium permanganate in water and dilute to 1000 ml. Set the solution aside for two weeks in a dark place, filter without washing through a fritted glass crucible and store in a dark-coloured stoppered bottle. Standardize the permanganate solution against standard sodium oxalate solution (see 16.2.7).

### 16.3 Procedure

**16.3.1** Depending upon the manganese content of the sample, transfer an accurately weighed sample and the volume of sodium hydroxide solution as given below to a 500-ml beaker:

<i>Manganese Content, Percent</i>	<i>Weight in g of the Sample to be Taken</i>	<i>Volume in ml of Sodium Hydro- xide Solution Required</i>
Over 1.0 up to 1.5	1	25
Over 0.25 up to 1.0	3	50
Over 0.1 up to 0.25	5	100

**16.3.2** Dissolve the sample as described under 15.3.2. Neutralize the solution with concentrated nitric acid and add 40 ml in excess. Boil the solution and add 0.5 g of sodium bismuthate. Boil for two to three minutes and dissolve the precipitated oxides of manganese in sufficient amount of sulphurous acid, added dropwise till solution is clear. Boil to expel oxides of sulphur and nitrogen. Dilute to about 100 ml with water and cool the solution to 10 to 15°C.

**16.3.3** Add about 0.5 g of sodium bismuthate (or 26 times more than manganese content of the sample but not less than 0.5 g). Agitate for 2 to 3 minutes and filter immediately through asbestos Gooch

crucible. Wash with cold dilute nitric acid until the washings are colourless. Reject the insoluble residue and maintain the temperature of the filtrate at 10 to 15° C. Add 2 ml of syrupy phosphoric acid to the measured excess of standard ferrous ammonium sulphate solution. Titrate immediately the excess of ferrous iron with the standard permanganate solution to the faint pink colour.

**16.3.4** Carry out a blank determination following the same procedure and using the same amount of the standard ferrous ammonium sulphate solution and other reagents as were used in the titration, but without the sample.

#### 16.4 Calculation

$$\text{Manganese, percent} = \frac{(A - B) C \times 1.1}{D}$$

where

*A* = volume in ml of the standard permanganate solution required to titrate the blank,

*B* = volume in ml of the standard permanganate solution required to titrate the excess of ferrous ammonium sulphate solution.

*C* = normality of the standard permanganate solution, and

*D* = weight in g of the sample taken.

### 17. DETERMINATION OF MAGNESIUM BY THE OXINE METHOD ( FOR MAGNESIUM CONTENT BETWEEN 0.01 TO 12 PERCENT )

**17.1 Outline of the Method** — After the removal of interfering elements, magnesium in the solution of the sample is precipitated with 8-hydroxyquinoline and determined either gravimetrically or volumetrically.

#### 17.2 Reagents

**17.2.1 Sodium Hydroxide** — solid.

**17.2.2 Hydrogen Peroxide** — 20 volumes.

**17.2.3 Sodium Carbonate** — solid.

**17.2.4 Sodium Carbonate Solution** — 5 g per litre.

**17.2.5 Methyl Red Indicator Solution** — see 13.2.7.

**17.2.6 Concentrated Ammonium Hydroxide** — 20 percent.

**17.2.7 Ammonium Chloride Wash Solution** — Dissolve 10 g of ammonium chloride in water, dilute to one litre, and make just yellow to methyl red with concentrated ammonium hydroxide.

**17.2.8 Ammonium Chloride** — solid.

**17.2.9 Concentrated Hydrochloric Acid** — see 6.2.9.

**17.2.10 Ammonium Sulphide Solution** — Saturate ammonium hydroxide (1 : 9) with hydrogen sulphide gas.

**17.2.11 Ammonium Persulphate** — solid

**17.2.12 Ammonium Sulphide Wash Solution** — Add 10 ml of ammonium sulphide solution to one litre of water containing 10 g of ammonium chloride and a few drops of ammonium hydroxide.

**17.2.13 Bromine Water** — saturated

**17.2.14 8-Hydroxyquinoline Solution** — Dissolve 5 g of 8-hydroxyquinoline in 10 ml of glacial acetic acid and dilute to 100 ml with water.

**17.2.15 Dilute Ammonium Hydroxide** — 1:99 (v/v).

**17.2.16 Methyl Orange Indicator Solution** — Dissolve 0.05 g of methyl orange in 100 ml of alcohol.

**17.2.17 Potassium Bromate-Potassium Bromide Solution** — Dissolve 2 g of potassium hydroxide, 80 g of potassium bromide, and 9 g of potassium bromate, in 700 ml of water and dilute to one litre.

**17.2.18 Potassium Iodide Solution** — 300 g per litre (w/v).

**17.2.19 Starch Solution** — see 11.2.13.

**17.2.20 Standard Potassium Iodate Solution** — 0.33 N. Dissolve 11.771 g of the potassium iodate dried at 180°C to constant weight in 200 ml of water, containing one gram of sodium hydroxide and add 10 g of potassium iodide; when solution is complete, dilute to one litre in a volumetric flask.

**17.2.21 Standard Sodium Thiosulphate Solution** — 0.33 N. Dissolve 81.84 g of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in one litre of freshly boiled and cooled water in a sterile glass bottle. Standardize as follows:

Pipette 25 ml of the standard potassium iodate solution (see 17.2.20) into a 125-ml flask. Add 30 ml of water, one gram of the potassium iodide and 10 ml of dilute sulphuric acid (1 : 4). Titrate with sodium thiosulphate solution to a light straw colour. Add 2 ml of starch solution and continue titration to the disappearance of the blue colour.

## 17.3 Procedure

**17.3.1** Depending upon the magnesium content of the sample, transfer an accurately weighed sample as given below to a 250-ml wide-mouthed Erlenmeyer flask:

<i>Magnesium Content, Percent</i>	<i>Weight in g of the Sample to be Taken</i>
Over 2.0	0.5 or less
Over 0.2 up to 2.0	1
Over 0.01 up to 0.2	2

It is recommended that for high magnesium content, such a weight of sample be taken that it does not contain more than 0.05 g of magnesium.

**17.3.2** Dissolve the sample in sodium hydroxide solution (*see Note 1*), using about 6 g of sodium hydroxide per g of the sample. After violent reaction has subsided, heat the flask to hasten the decomposition of the sample. When visible evolution of hydrogen ceases, cautiously add few drops of hydrogen peroxide to the hot concentrated solution to complete the oxidation of silicon, zinc and chromium (*see Note 2*). Dilute to 150 ml and add 3 to 5 g of sodium carbonate. Stir well, and allow the precipitate to settle. Filter and wash the residue with hot sodium carbonate solution. Dissolve the magnesium in the residue, into original container, with 40 ml of dilute hydrochloric acid (1:1) and wash the filter with hot water.

**NOTE 1** — In case of high silicon alloys, sample should be first attacked with weak alkali and subsequently to strong alkali. By the former treatment, aluminium will dissolve almost completely and with the latter treatment silicon will dissolve without precipitation of silicates.

**NOTE 2** — If chromium-bearing constituents are not completely decomposed, an insoluble residue containing some magnesium will remain after treatment with concentrated hydrochloric acid.

**17.3.3** If the sample does not contain manganese, nickel or more than 3 mg of copper, add few drops of methyl red indicator and then add concentrated ammonium hydroxide and about 5 g of ammonium chloride until the solution is yellow to methyl red. Allow the precipitate to coagulate, filter and wash with hot ammonium chloride wash solution. If the magnesium content is over 0.02 g, place the paper with the precipitate in the original container and dissolve with 15 ml of dilute hydrochloric acid. Dilute to 50 ml with hot water. Precipitate as before, filter and wash with hot ammonium chloride wash solution. Make the combined filtrate just acid to methyl red and precipitate magnesium as before.

**17.3.4** In case the sample contains manganese, nickel and more than 3 mg of copper, neutralize the acid solution as obtained under **17.3.2** with concentrated ammonium hydroxide and add about 5 g of ammonium chloride. Add 5 ml of ammonium sulphide solution (see Note). Filter into a 250-ml beaker, and wash with ammonium sulphide wash solution. If more than 20 mg of magnesium are present in the sample, some magnesium may be carried down with the sulphides. In that case, dissolve the precipitate with 15 ml of dilute hydrochloric acid and re-precipitate as under **17.3.3**. Filter and wash the sulphides. Combine the filtrates and boil vigorously to drive off the ammonium sulphide. If a noticeable sulphide precipitate forms as the solution boils and becomes acid (usually indicating nickel or tin), filter, wash and boil the filtrate. Oxidize the remaining sulphur by adding an excess of bromine water, and continue boiling until the colour disappears.

**NOTE** — In case of alloys with manganese content over one percent, manganese may not completely precipitate by ammonium sulphide. In that case, add a few grams of ammonium persulphate to the filtrate to separate manganese completely.

**17.3.5** Adjust the volume of the solution obtained under **17.3.3** or **17.3.4** to 75 ml. Remove from the hot plate, add 10 ml of bromine water, and while stirring make the solution alkaline with concentrated ammonium hydroxide and add 15 drops in excess. Digest until any manganese present precipitates as manganese dioxide, keeping the solution ammoniacal. Stir just as the solution begins to boil to aid coagulation. Filter and wash with hot water.

**17.3.6** Make the filtrate acidic to methyl red with concentrated hydrochloric acid. If the indicator does not hold its colour, boil the solution until the bromine is gone. Make the volume of the solution to about 150 ml, neutralize the solution with concentrated ammonium hydroxide. Add 5 g of ammonium acetate and 4 g of acetic acid. Warm to 70°C, treat with slight excess of oxine solution. Filter and to the filtrate add concentrated ammonium hydroxide in excess. Add 5 ml of oxine solution, while stirring (5 ml is enough for 0.015 g of magnesium; for larger amounts of magnesium up to 0.03 g, add 10 ml). Heat the solution just to boiling, remove from the source of heat and allow to stand for 15 to 20 minutes. Filter and wash with hot dilute ammonium hydroxide. Since only magnesium oxinate is present, the amount may be determined either gravimetrically or volumetrically as described under **17.3.7** and **17.3.8** respectively.

**17.3.7 Gravimetric Method** — Filter the magnesium oxinate precipitate on a weighed sintered-glass funnel, washing with hot weakly ammoniacal water, dry at 100 to 105°C and weigh as the dihydrate. If the quantity of the quinolate is small, proceed as under **17.3.8**.



**17.3.7.1 Calculation**

$$\text{Magnesium, percent} = \frac{A}{B} \times 6.98$$

where

$A$  = weight in g of the oxinate, and

$B$  = weight in g of the sample taken.

**17.3.8 Volumetric Method** — Dissolve the precipitate of oxinate as obtained under 17.3.7 into a 400-ml stoppered bottle using 30 ml of hot dilute hydrochloric acid. Wash with cold dilute hydrochloric acid (90 ml of water plus 35 ml of dilute hydrochloric acid) and then with hot water so as to give an acid ratio of 1 : 4 at a volume of approximately 150 ml. Add a few drops of methyl orange indicator solution. Run in potassium bromate-potassium bromide solution from a burette, until the indicator is decolourized (indicating that bromate is present in excess) and add 5 ml more. Note the volume of the potassium bromate-potassium bromide solution added. Then add 10 ml of potassium iodide solution. Titrate immediately with the standard sodium thiosulphate solution using 2 ml of starch solution as an indicator near the end of the titration. The time from the addition of potassium bromate-potassium bromide solution to the end of the titration should not exceed 2 minutes.

**17.3.8.1** Carry out a blank using the same quantity of the reagents. Titrate the blank through each step of procedure.

**17.3.8.2 Calculation**

$$\text{Magnesium, percent} = \frac{(A-B) C \times 0.3}{D}$$

where

$A$  = volume in ml of the standard sodium thiosulphate solution required to titrate the blank,

$B$  = volume in ml of the standard sodium thiosulphate solution required to titrate the sample,

$C$  = normality of the standard sodium thiosulphate solution, and

$D$  = weight in g of the sample taken.

## 18. DETERMINATION OF MAGNESIUM BY THE ETHYLENEDIAMINE TETRA-ACETATE METHOD (FOR MAGNESIUM CONTENT BETWEEN 0.5 TO 11 PERCENT)

**18.1 Outline of the Method** — After the separation of manganese, iron etc., magnesium in the solution is titrated against standard sodium ethylenediamine tetra-acetate solution using chrome Black T as indicator. The

interference due to calcium is not quantitative and has, therefore, been ignored. Potassium cyanide is added to the solution to complex zinc, copper and nickel.

## 18.2 Reagents

**18.2.1 Sodium Hydroxide Solution** — 20 percent (w/v). Dissolve 200 g of sodium hydroxide in water in a beaker. Cool, transfer to a plastic (polythene) bottle, and dilute to one litre.

**18.2.2 Hydrogen Peroxide** — 20 volumes.

**18.2.3 Potassium Cyanide Solution** — 250 g/litre.

**18.2.4 Dilute Hydrochloric Acid** — 1:1 (v/v).

**18.2.5 Potassium Cyanide Solution** — 200 g/l.

**18.2.6 Dilute Hydrochloric Acid** — 1:1 (v/v).

**18.2.7 Ammonium Chloride** — solid.

**18.2.8 Bromine Water** — saturated.

**18.2.9 Concentrated Ammonium Hydroxide** — 20 percent.

**18.2.10 Sodium Acetate** — solid.

**18.2.11 Tartaric Acid**

**18.2.12 Chrome Blank T Indicator** — Dissolve 0.5 g of chrome Black T, colour index 203 and 4.5 g of hydroxylamine hydrochloride in 100 ml of alcohol. Store in a glass stoppered bottle. This solution is stable for at least two months.

**18.2.13 Standard Magnesium Solution** ( $1 \text{ ml} = 0.001 \text{ of Mg}$ ) — Dissolve one gram of pure magnesium turnings in 25 ml of dilute sulphuric acid (1:4) or 10.135 g of hydrated magnesium sulphate in water and dilute to one litre.

**18.2.14 Standard EDTA Solution** ( $1 \text{ ml} = 0.0011 \text{ g of Mg}$ ) — Dissolve 17.1 g of sodium ethylenediamine tetra-acetate dihydrate in water and dilute to one litre. Standardize as follows:

Transfer a 20 ml aliquot of standard magnesium solution (see 18.2.13) to a 400-ml beaker. Add 40 ml of dilute hydrochloric acid (1:1) and neutralize with concentrated ammonium hydroxide. Dilute to 250 ml with water, add 70 ml of concentrated ammonium hydroxide and continue according to the procedure given under 18.3.

### 18.3 Procedure

**18.3.1** Transfer 0.5 to 1.0 g of the accurately weighed sample to a 250-ml beaker. Add 30 ml of sodium hydroxide solution. When the reaction subsides, wash down the sides of the beaker with a little water and boil until the reaction ceases. Add a few drops of hydrogen peroxide followed by 5 ml of potassium cyanide solution and boil. Dilute to about 150 ml with hot water and filter through a hardened rapid filter paper, washing the walls with hot water.

**18.3.2** Dissolve the precipitate on the filter with 40 ml of hot dilute hydrochloric acid catching the solution in the original 250-ml beaker and washing the paper well with hot water. Add 6 to 8 g of ammonium chloride and 5 ml of bromine water; bring to boil for one or two minutes and add sufficient concentrated ammonium hydroxide to decolorize the solution (3 ml approximately). Finally add 20 ml of bromine water, two to three grams of sodium acetate and a pinch of pulp and boil for a further one or two minutes. Avoid a large excess of concentrated ammonium hydroxide to prevent solution of any aluminium which otherwise would interfere with the end point in the subsequent titration. Bring to the boil to coagulate the precipitated manganese dioxide and boil for at least 5 minutes to expel excess ammonia. Allow to settle for a minute and filter through a paper with pulp, collecting the filtrate in a 400-ml beaker. Wash well with hot water (if the manganese content is high in the sample under test, no dilution and precipitation as before). Cool the filtrate to room temperature and adjust it to pH 10 by adding 70 ml of concentrated ammonium hydroxide.

**18.3.3** Make alkaline with an excess of concentrated ammonium hydroxide (10 drops). Add 5 to 10 ml of potassium cyanide solution, 7 to 10 drops of Eriochrome Black T indicator and titrate with standard EDTA solution.

**18.3.4 Blank Determination** — Neutralize 40 ml of dilute hydrochloric acid with concentrated ammonium hydroxide, dilute to 250 ml with water and add 70 ml of concentrated ammonium hydroxide. Titrate the blank according to the procedure given under 18.3.3.

### 18.4 Calculation

$$\text{Magnesium, percent} = \frac{(A - B) C}{D} \times 100$$

where

**A** = volume in ml of EDTA solution required to titrate the sample,

**B** = volume in ml of EDTA solution required to titrate the blank,

$C$  = magnesium equivalent of the EDTA solution in g/ml, and

$D$  = weight in g of the sample taken.

## 19. DETERMINATION OF NICKEL BY THE DIMETHYLGLYOXIME (GRAVIMETRIC) METHOD

**19.1 Outline of the Method** — After removal of the interfering elements nickel in the solution of the sample is precipitated in ammoniacal medium by dimethylgly oxime, filtered, washed dried and weighed.

### 19.2 Reagents

**19.2.1 Sodium Hydroxide Solution** — 20 percent (w/v).

**19.2.2 Dilute Hydrochloric Acid** — 1:1 (v/v).

**19.2.3 Concentrated Nitric Acid** — see 6.2.6.

**19.2.4 Dilute Sulphuric Acid** — 1:1 (v/v).

**19.2.5 Hydrogen Sulphide** — gas.

**19.2.6 Hydrogen Sulphide Wash Solution** — Saturate dilute sulphuric acid (1:99) with hydrogen sulphide.

**19.2.7 Tartaric Acid Solution** — Dissolve 25 g of tartaric acid in 60 ml of water, filter, add one ml of concentrated nitric acid and dilute to 100 ml.

**19.2.8 Ammonium Chloride** — solid.

**19.2.9 Concentrated Ammonium Hydroxide** — 20 percent.

**19.2.10 Dimethylglyoxime Solution** — Dissolve one gram of dimethylglyoxime in 100 ml of concentrated ammonium hydroxide and filter.

### 19.3 Procedure

**19.3.1** Depending upon the nickel content of the sample, transfer an accurately weighed sample and the volume of alkali as given below to a beaker:

Nickel Content, Percent	Weight in g of the Sample to be Taken	Volume in ml of Sodium Hydroxide Solution Required
Over 0.5 up to 4	2	20
Over 0.1 up to 0.5	5	40
Less than 0.1	10	100

**19.3.2** Dissolve the sample in the required amount of sodium hydroxide solution. When the reaction is complete, dilute to 150 ml with hot water, allow the residue to settle for a short time, filter and wash with hot water. Dissolve the residue with a minimum amount of hot dilute hydrochloric acid together with a little concentrated nitric acid, wash the paper thoroughly with hot water. Add 10 ml of dilute sulphuric acid, evaporate to dense white fumes, dilute to 100 ml with hot water, and saturate with hydrogen sulphide gas, filter and wash with hydrogen sulphide wash solution.

**19.3.3** Boil the filtrate to remove the hydrogen sulphide gas, add 5 ml of concentrated nitric acid, and boil to oxidize iron. Dilute to 200 ml, add 10 ml of tartaric acid solution and 5 g of ammonium chloride. Neutralize with concentrated ammonium hydroxide. Acidify with dilute hydrochloric acid. Heat nearly to boiling and while stirring add dimethylglyoxime solution (20 ml for amounts of nickel up to 0.02 g and 5 ml for each additional 0.01 g). Allow to stand for one hour. Filter and wash with cold water. Dry the precipitate at 110 to 120°C to constant weight. Cool in a dessicator and weigh as nickel dimethylglyoxime.

#### 19.4 Calculation

$$\text{Nickel, percent} = \frac{A \times 20.32}{B}$$

where

$A$  = weight in g of nickel dimethylglyoxime, and

$B$  = weight in g of the sample taken.

### 20. DETERMINATION OF CHROMIUM BY THE PERSULPHATE OXIDATION (VOLUMETRIC) METHOD

**20.1 Outline of the Method** — Chromium is oxidized to chromate by means of ammonium persulphate in presence of silver nitrate and potassium permanganate formed is destroyed with hydrochloric acid. It is then reduced with a measured volume of ferrous ammonium sulphate solution and the excess ferrous solution is titrated with standard permanganate solution.

#### 20.2 Reagents

**20.2.1 Concentrated Sulphuric Acid** — see 6.2.3.

**20.2.2 Concentrated Nitric Acid** — see 6.2.6.

**20.2.3 Sulphuric Acid-Nitric Acid Mixture** — Slowly stir 100 ml of concentrated sulphuric acid into one litre of water, cool, and add 400 ml of concentrated nitric acid, dilute to two litres.

**20.2.4 Silver Nitrate Solution** — 8 g per litre.

**20.2.5 Hydrofluoric Acid** — 40 percent.

**20.2.6 Ammonium Persulphate** — solid.

**20.2.7 Dilute Hydrochloric Acid** — 1 : 1 ( v/v ).

**20.2.8 Standard Ferrous Ammonium Sulphate Solution** — 0.03 N. Dissolve 3.2 g of  $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$  in 500 ml of cold dilute sulphuric acid ( 5:95 ) and dilute to one litre with this sulphuric acid. Standardize against recrystallized potassium dichromate solution.

**20.2.9 Standard Potassium Permanganate Solution** — 0.03 N. Dissolve 3.2 g of potassium permanganate in one litre of water. Store in a dark coloured glass stoppered bottle. Standardize against pure re-crystallized sodium oxalate or oxalic acid.

### 20.3 Procedure

**20.3.1** Transfer one gram of the accurately weighed sample to a 400-ml beaker, add 30 ml of the sulphuric acid-nitric acid mixture and 20 ml of silver nitrate solution. Heat gently until the sample is dissolved. If free silicon is present, add a few drops of hydrofluoric acid. Boil until brown fumes have been expelled.

**20.3.2** Dilute to 300 ml with hot water, add 2 g of ammonium persulphate and heat to boiling. After the chromium is oxidized, boil for 10 minutes. Add 0.5 ml of dilute hydrochloric acid and continue boiling until any manganese present is reduced. If necessary add additional 0.5 ml portions of dilute hydrochloric acid and boil for 15 minutes after the final addition.

**20.3.3** Cool and add a measured volume of ferrous ammonium sulphate solution until colour changes from yellow to green ( 7 ml will reduce about 0.01 g of chromium ). Titrate with standard potassium permanganate solution until a faint pink end point is obtained that persists for one minute.

### 20.4 Calculation

$$\text{Chromium, percent} = \frac{(AB - CD) \times 1.734}{E}$$

where

*A* = volume in ml of the standard ferrous ammonium sulphate solution used,

*B* = normality of the standard ferrous ammonium sulphate used,

$C$  = volume in ml of the standard potassium permanganate solution used,

$D$  = normality of the standard potassium permanganate solution used, and

$E$  = weight in g of the sample taken.

## 21. DETERMINATION OF TIN BY THE IODOMETRIC METHOD

**21.1 Outline of the Method** — Tin in the sample is completely dissolved in hydrochloric acid in the presence of antimony. Stannous chloride thus formed is titrated with standard potassium iodate solution in carbon dioxide atmosphere.

**20.2 Apparatus** — A 500-ml conical flask fitted with a three-holed rubber stopper containing an inlet tube for carbon dioxide, an air condenser, and a hole for a burette that shall be kept closed by means of a glass rod until the titration is started. During the reduction, a very slow stream of carbon dioxide shall be passed through the flask. When the reduction is complete, the flow shall be increased to maintain a protective cover of carbon dioxide during cooling and titration ( *see Fig. 2* ).

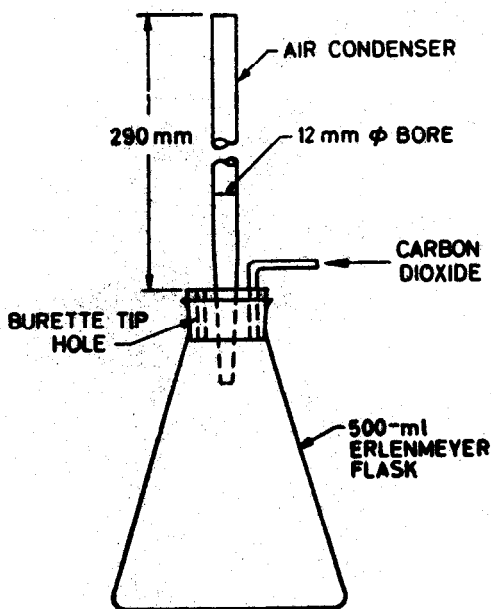


FIG. 2 APPARATUS FOR REDUCTION OF TIN

### 21.3 Reagents

**21.3.1 Antimony** — Metallic powder.

**21.3.2 Aluminium Sheet or Rolled Foil** — Tin free.

**21.3.3 Dilute Hydrochloric Acid** — 1:2 ( v/v ).

**21.3.4 Carbon Dioxide** — gas.

**21.3.5 Starch-Potassium Iodide Solution** — Make a paste of one gram of soluble starch in about 5 ml of water and add to 100 ml of boiling water, cool, and add 40 g of potassium iodide and stir until the potassium iodide is dissolved. Prepare fresh as needed.

**21.3.6 Standard Potassium Iodate Solution** — 0.025 N. Dissolve 0.892 g of potassium iodate ( dried at 180°C ) in 200 ml of water, containing one gram of sodium hydroxide and add 10 g of potassium iodide, when solution is complete, dilute to one litre in a volumetric flask. Standardize against tin solution as prepared under 21.3.7.

**21.3.7 Standard Tin Solution** — Dissolve one gram of tin in a covered 400-ml beaker in 300 ml of dilute hydrochloric acid ( 1:1 ) by warming gently until the metal has dissolved. If the solution is difficult, add 0.05 to 0.1 g of potassium chlorate. Cool and dilute to one litre in a volumetric flask.

### 21.4 Procedure

**21.4.1** Transfer 2 to 5 g of the accurately weighed sample to a 500-ml flask and add 0.25 g of powdered antimony and 150 ml of dilute hydrochloric acid. After the reaction slackens, heat the flask finally, boiling for about 10 minutes to ensure complete solution of tin. Filter and wash with dilute hydrochloric acid. Discard the residue and return the filtrate to the original flask.

**21.4.2** Add 0.25 g of powdered antimony and 0.5 g of aluminium sheet or rolled foil free from tin. ( If silicon content is low then the addition of aluminium may not be required ). Stopper the flask and assemble the apparatus as shown in Fig. 2. Start passing slow current of carbon dioxide gas through the flask. Heat gently until the aluminium is completely dissolved and boil for 10 minutes. Increase the flow of the gas enough to prevent back pressure and cool. As soon as cold, with the current of carbon dioxide gas still passing, open the stoppered-hole and add from a pipette 5 ml of fresh starch potassium iodide solution. Insert the tip of the burette containing standard potassium iodate solution of suitable strength and titrate to a blue colour.

**21.4.3** Carry out a blank determination, following the same procedure and using the same amounts of all reagents, but without the sample.



## 21.5 Calculation

$$\text{Tin, percent} = \frac{(A - B) C}{D} \times 100$$

where

*A* = volume in ml of the standard potassium iodate solution required to titrate the sample,

*B* = volume in ml of the standard potassium iodate solution required to titrate the blank,

*C* = tin equivalent of the standard potassium iodate solution in g/ml, and

*D* = weight in g of the sample taken.

## 22. DETERMINATION OF ANTIMONY BY THE POTASSIUM IODIDE-THIOUREA (PHOTOMETRIC) METHOD

**22.1 Outline of the Method** — In acid solution of the sample, a strong yellow colour is produced by the addition of excess potassium iodide. In the presence of thiourea, copper is kept in solution as a colourless complex.

NOTE — Interference due to bismuth is ignored as this chemical is normally not found in aluminium alloys.

### 22.2 Reagents

**22.2.1 Sodium Hydroxide Solution** — 40 percent (w/v).

**22.2.2 Dilute Sulphuric Acid** — 1 : 1 (v/v).

**22.2.3 Dilute Nitric Acid** — 1 : 1 (v/v).

**22.2.4 Hydrazine Sulphate** — solid.

**22.2.5 Thiourea** — solid.

**22.2.6 Potassium Iodide Solution** — 50 percent (w/v).

**22.2.7 Standard Antimony Solution** — Dissolve 2.0337 g of potassium antimonious tartarate (dried at 100°C for an hour) in 100 ml of concentrated hydrochloric acid and make up to one litre. (Check the antimony content by iodimetric titration.) Alternatively dissolve 0.400 g of pure antimony in aqua regia, add 100 ml of concentrated hydrochloric acid and make up to one litre.

### 22.3 Procedure

**22.3.1** Dissolve 0.40 g of an accurately weighed sample in 10 ml of sodium hydroxide solution. Warm and after the attack is complete add

15 ml of dilute sulphuric acid followed by 10 ml of dilute nitric acid. Boil, cool for about one minute. Add 0.25 g of hydrazine sulphate to reduce ferric iron to ferrous state. Boil for two minutes, cool to room temperature and transfer to a 200-ml volumetric flask. Add 2 to 3 g of thiourea followed by 40 ml of potassium iodide solution. Make up to the mark and mix.

**22.3.2** Take a suitable aliquot, filter through filter paper No. 3, transfer to an absorption cell and adjust the photometer to the initial setting. Take the photometric readings using a light filter at approximately 15 minutes after the addition of thiourea as otherwise turbidity by decomposition of thiourea may occur.

**22.3.3 Calibration Curve** — Take a series of standard antimony solutions and a reagent blank. Using the same quantities of reagents, carry through all the stages as described under **22.3.1** and **23.3.2** and record the photometric readings of the standard solutions along with the blank. Draw calibration curve by plotting the photometric readings of standard solutions against milligrams of antimony per 100 ml of the solution.

**22.4 Calculation** — Convert the photometric readings of the sample to milligrams of antimony by means of calibration curve and calculate the percentage of antimony as follows:

$$\text{Antimony, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$  = weight in mg of antimony found in the sample represented by the aliquot solution used, and

$B$  = weight in g of the sample represented by the aliquot taken.

## 23. DETERMINATION OF TITANIUM BY THE HYDROGEN PEROXIDE (PHOTOMETRIC) METHOD

**23.1 Outline of the Method** — The sample is subjected to the action of sodium hydroxide and acidified with nitric acid-sulphuric acid mixture. The yellow-coloured complex produced in acid solution of the sample by the addition of hydrogen peroxide is determined photometrically at approximately 410 m $\mu$ .

### 23.2 Reagents

**23.2.1 Sodium Hydroxide Solution** — 20 percent (w/v).

**23.2.2 Nitric Acid-Sulphuric Acid Mixture** — Add 50 ml of concentrated nitric acid (see **6.2.6**) to 600 ml of water; then add 350 ml of concentrated sulphuric acid (see **6.2.3**) slowly, while stirring and cool the mixture.

**23.2.3 Dilute Sulphuric Acid** — 1 : 9 ( v/v ).

**23.2.4 Hydrogen Peroxide** — 20 volumes.

**23.2.5 Standard Titanium Solution** — ( 1 ml = 0.000 15 g of Ti ). Fuse 2.25 g of titania in a covered crucible with 15 g of potassium pyrosulphate and dissolve the cold melt in 200 ml of hot dilute sulphuric acid ( 1 : 1 ). Cool to room temperature and dilute to one litre in a volumetric flask.

### 23.3 Procedure

**23.3.1** Transfer one gram of the accurately weighed sample to a 400-ml beaker, cover and add in small instalments 30 ml of sodium hydroxide solution. When the reaction subsides, wash down the cover and sides of the beaker, boil to complete the reaction and cool. Add 50 ml of nitric acid-sulphuric acid mixture, boil to dissolve salts, expel brown fumes and cool. Transfer to a 100-ml volumetric flask. Dilute to the mark and mix. Filter through a dried fine paper discarding the first few millilitres of filtrate. Preserve the filtrate.

**23.3.2** Transfer a suitable aliquot from 25 ml portion of the solution reserved under **23.3.1**, to an absorption cell and adjust the photometer to the initial setting, using a light filter at approximately 410 m $\mu$ . To the rest of remaining portion of the filtrate reserved under **23.3.1**, add few drops of phosphoric acid and two drops of hydrogen peroxide and mix. While maintaining the photometer adjustment, take the photometric reading of a suitable portion of the solution.

**23.3.3 Calibration Curve** — Take a series of standard titanium solutions and the reagent blank. Using the same quantities of the reagents carry through all the stages as described under **23.3.2**. Record the photometric readings of the standard solutions along with the blank. Draw a calibration curve by plotting the photometric reading of the standard solutions against milligrams of titanium per 100 ml of the solution.

**23.4 Calculation** — Convert the photometric readings of the sample and the blank solutions to milligrams of titanium by means of the calibration curve. Calculate the percentage of titanium as follows:

$$\text{Titanium, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$  = weight in mg of titanium found, and

$B$  = weight in g of the sample taken.